

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT: N00014-91J-0201

R&T CODE: 4133032

Robert J. Nowak

TECHNICAL REPORT NO. 52

by G. L. Homyak, C. J. Patrissi and C. R. Martin

Prepared for Publication

in

Nanostructured Materials

Colorado State University  
Department of Chemistry  
Fort Collins, CO 80523-1872

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REPORT DOCUMENTATION PAGE

2. September 30 , 1996

3. Interim report

4. "Finite Sized Oblate and Ortho-Prolate Metal Nanoparticles: Optical Theory and Potential as Surface Enhanced Raman Spectroscopic Substrates "

5. GRANT: N00014-91J-0201 , R&T CODE: 4133032

6. G. L. Hornyak, C. J. Patrissi and Charles R. Martin

7. Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872

8. TECHNICAL REPORT NO. 52

9. Office of Naval Research, Chemistry Division, 800 North Quincy Street, Arlington, VA 22217-5660

11. To be published in Nanostructured Materials

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13. Abstract: The relative absorption intensities of composites containing Au, Ag or Cu prolate ( $a>b=c$ ), oblate ( $a<b=c$ ), ortho-prolate ( $b>a=c$ ) and ortho-oblate ( $b<a=c$ ) nanoparticles have been modeled with the dynamical Maxwell-Garnett effective medium expression. The electric field of the light was along the b-axis of the nanoparticles in simulations. The semi-radii b for prolate-oblate particles and a for the ortho counterparts were equal to 26 nm. The results of simulations indicate that the absorptive power of the composites increased as particle shape changed from ortho-oblate  $\rightarrow$  ortho-prolate and prolate  $\rightarrow$  oblate. We found that in simulations, ortho-prolate particles provided the greatest intensity per unit volume fraction of metal. When considering particle shape only, the degree of enhancement expected from SERS substrates is approximately proportional to the intensity of absorption. We also propose a simple means of fabricating SERS substrates by means of the template synthesis method.

14. Subject terms: Nanomaterials, nanometals, optical properties

17. 18. 19. Unclassified

## FINITE SIZED OBLATE AND ORTHO-PROLATE METAL NANOPARTICLES: OPTICAL THEORY AND POTENTIAL AS SURFACE ENHANCED RAMAN SPECTROSCOPIC SUBSTRATES

G.L. Hornyak, C.J. Patrissi and C. R. Martin

Dept. of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

*Abstract* - - The relative absorption intensities of composites containing Au, Ag or Cu prolate ( $a > b = c$ ), oblate ( $a < b = c$ ), ortho-prolate ( $b > a = c$ ) and ortho-oblate ( $b < a = c$ ) nanoparticles have been modeled with the dynamical Maxwell-Garnett effective medium expression. The electric field of the light was along the  $b$ -axis of the nanoparticles in simulations. The semi-radii  $b$  for prolate-oblate particles and  $a$  for the ortho counterparts were equal to 26 nm. The results of simulations indicate that the absorptive power of the composites increased as particle shape changed from ortho-oblate  $\rightarrow$  ortho-prolate and prolate  $\rightarrow$  oblate. We found that in simulations, ortho-prolate particles provided the greatest intensity per unit volume fraction of metal. When considering particle shape only, the degree of enhancement expected from SERS substrates is approximately proportional to the intensity of absorption. We also propose a simple means of fabricating SERS substrates by means of the template synthesis method.

### INTRODUCTION

The optical properties of nanometals depend strongly on particle size, shape and orientation when exposed to a photon field. The giant electromagnetic enhancements associated with SERS are related to the aforementioned criteria but are also dependent on the type of metals found in these substrates. Our goals in this short study are twofold: first, we wish to model the absorptive power of low but equivalent volume fraction composites in which nanometal shape and orientation are varied mathematically by means of effective medium theories; and secondly, to proceed beyond the single particle models (1) in which particle-particle interactions are not taken into account. In the future, we will present electromagnetic models of true SERS substrates which consist of much higher metal fraction (beyond the percolation limit) with thin optical layers ( $d_2$ ) in which topological considerations are taken into account.

Particles of finite size which are not small compared to the wavelength of the analytical beam and are insulated from one another can be modeled by the dynamical version of the Maxwell-Garnett effective medium expression (DMG) (1). The expression is given below in which the dielectric function of the composite,  $\bar{\epsilon}_c$ , is related to the components.

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$$\frac{\bar{\epsilon}_c - \bar{\epsilon}_m}{\bar{\epsilon}_c + \kappa_{\text{eff}} \bar{\epsilon}_m} = f_p \left( \frac{\bar{\epsilon}_p - \bar{\epsilon}_m}{\bar{\epsilon}_p + \kappa_{\text{eff}} \bar{\epsilon}_m} \right)$$

$\bar{\epsilon}_p$ , and  $\bar{\epsilon}_m$  are the wavelength dependent dielectric functions of the composite, the metal particles and the surrounding insulating medium respectively.  $f_p$  is the volume fraction of the metal filling factor and  $\kappa_{\text{eff}}$  is the dynamic screening parameter which is wavelength, size and shape dependent. A summary of the values of the shape component of  $\kappa_{\text{eff}}$ , symbolized by  $\kappa$  the static screening parameter, is shown in Figure 1. The complete SERS enhancement factor for infinitely small spherical

$$G = \left( \frac{\bar{\epsilon}_p - \bar{\epsilon}_m}{\bar{\epsilon}_p + 2\bar{\epsilon}_m} \right)_\lambda^2 \left( \frac{\bar{\epsilon}_p - \bar{\epsilon}_m}{\bar{\epsilon}_p + 2\bar{\epsilon}_m} \right)_S^2 X^{12}$$

where  $\lambda$  and  $S$  represent the laser and Stokes fields. For spheres,  $X = r/(r+d)$  where  $r$  is the sphere radius and  $d$  the distance of the molecule from the surface (2). The 2 represents the value of the screening parameter for a sphere (Figure 1). For particles that are not small or necessarily spherical, the 2 is replaced by  $\kappa_{\text{eff}}$  and  $X$  is modified to accommodate ellipsoidal shapes. Absorption and resonance enhancement are maximized in both equations when the RHS denominators are zeroed.

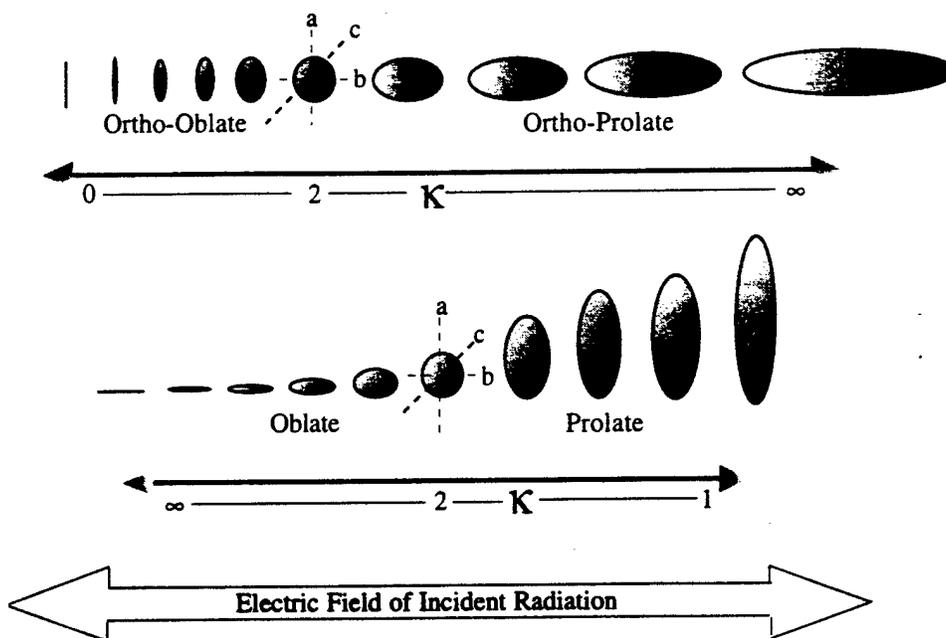


Figure 1. Static screening parameter and particle shape.

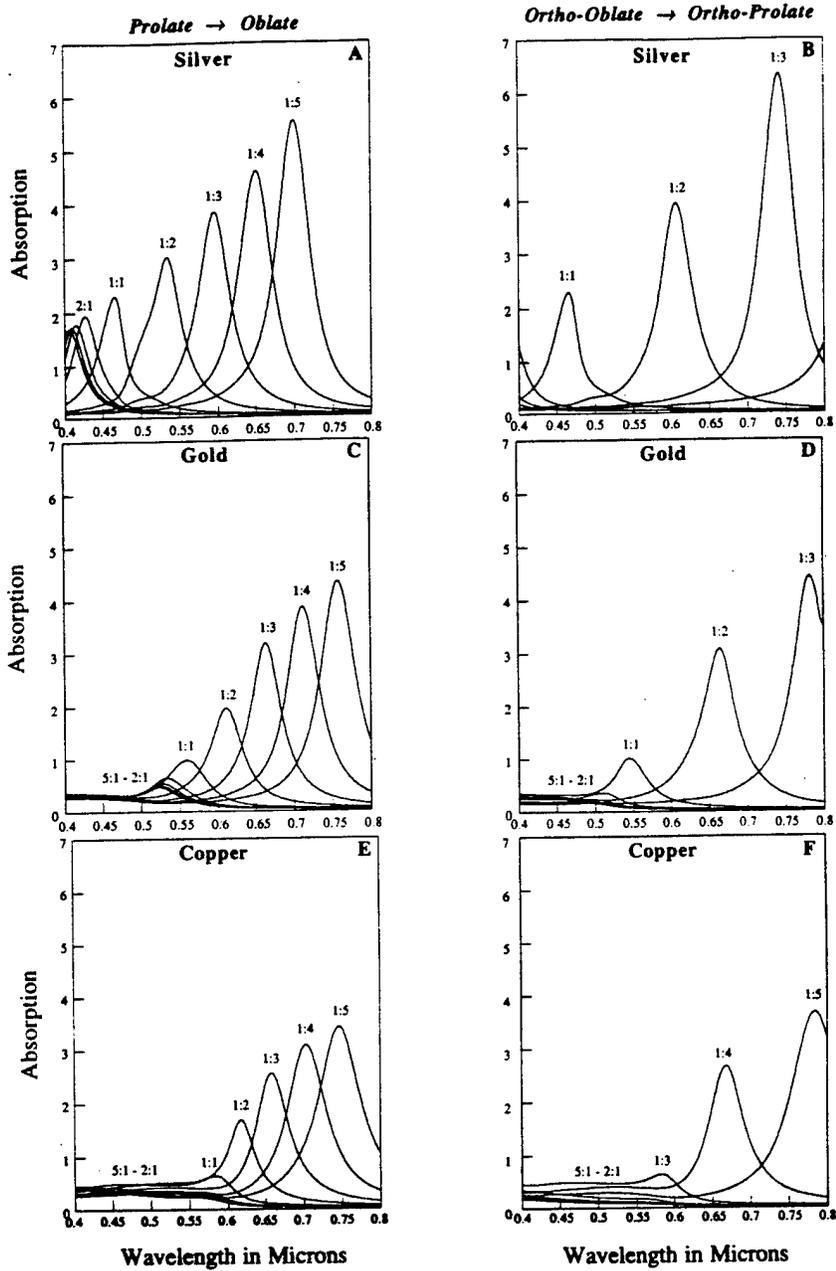


Figure 2. Absorptive power of nanometal composites. Aspect ratio is represented by numbers on top of peaks. Note that ortho-prolate particle composites with AR of 1:3 possess higher absorption intensity than oblate ones with AR of 1:5.

The input parameters for DMG were as follows:  $f_p = 0.01$ ,  $d_2 = 1 \mu\text{m}$ ,  $b = 26$  nm for ellipsoidal prolate, spherical and oblate particles and,  $a = 26$  nm for ortho-counterparts; orientation of photon field was along  $b$  and the refractive index of insulating medium was  $\approx 1.5$ . Particle aspect ratio was varied from 1 to 5. Optical constant data bases of Au, Ag and Cu were taken from the literature.

## DISCUSSION

The absolute absorption profiles of composites containing prolate  $\rightarrow$  oblate (A,C,E) and ortho-prolate  $\rightarrow$  ortho-oblate (B,D,F) of various particle aspect ratio for Au, Ag and Cu are shown in Figure 2. Absorption intensity with respect to particle shape increased in the following order: ortho-oblate  $\rightarrow$  prolate  $\rightarrow$  spherical  $\rightarrow$  oblate  $\rightarrow$  ortho-prolate. In DMG and from Figure 1, particle shapes in which the static screening parameter  $\kappa$  was large are most suitable for use in SERS. Large  $\kappa$  correspond to oblate and ortho-prolate particle shapes. However, larger  $\kappa$  can result in red shifts in the absorption maximum of the composite and care must be taken so as not to exceed the wavelength range of the excitation source. This is shown in Figure 2 as lower aspect ratio ortho-prolate particles are more red-shifted than higher aspect ratio oblate particle composites. The best shapes for SERS substrates were obviously the oblate and the ortho-prolate. Silver showed the best potential as a SERS substrate material.

Both oblate and ortho-prolate particles can be fabricated by means of the template synthesis method using porous aluminum oxides as the template material (1). Oblate particles are fabricated directly. Ortho-prolate particles can be reoriented by friction. The template method is a low cost means of forming nanostructured materials as no high vacuum equipment or expensive lasers are required.

## CONCLUSIONS

Absorption intensity of nanometal composites can be used to study the effectiveness of particles with specific shape to be employed in SERS substrates. In the qualitative sense, the results derived by DMG agree with the order of absorptive power (and therefore enhancement) with those determined by means of the single particle model (3):  $\text{Ag} > \text{Au} > \text{Cu}$ . Ag is considered to be the best substrate material for SERS and ortho-prolate particles would provide the best enhancement. Ortho-oblate particles generate absorptions that are nearly undetectable. We did not present the relationship between particle size and absorption intensity, but we have determined by means of DMG that absorption increases as particle size decreases. We wish to thank the Office of Naval Research (ONR), Grant #: N00014-93-1-0945, for providing funding.

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